

# **D R A F T**

## **REMEDIATION AND BENEFICIAL REUSE OF PCB-CONTAINING WASTES USING THE CEMENT-LOCK™ TECHNOLOGY**

**FINAL REPORT  
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## EXECUTIVE SUMMARY

This report presents the results of an experimental program conducted by the Institute of Gas Technology (IGT) under a contract with the Gas Research Institute (GRI) for "Remediation and Beneficial Reuse of PCB-Containing Wastes Using the Cement-Lock™ Technology." The overall objectives of the program were to determine the extent of PCB destruction in PCB-containing wastes by IGT's Cement-Lock Technology, to determine the fate of chlorine present in PCB, and to produce a beneficial use product, namely, construction-grade cement, from the waste. Construction Technology Laboratories, Inc. (the research arm of the Portland Cement Association) was a subcontractor to IGT on this program, specifically for evaluating the properties of the cement produced.

A bench-scale unit was set up for conducting PCB destruction and chlorine sequestration tests. Methylene chloride (dichloromethane) was used as a surrogate for PCB. The methylene chloride was conveyed into the reactive melt chamber with a carrier gas that consisted of a mixture of natural gas and air such that the combustion product gas contained about 3 percent oxygen. The resultant product gas mixture was bubbled through a molten reactive mixture of inorganic compounds representative of the Cement-Lock process. A temperature of about 2700°F was maintained in the reactor. The product gas was then passed through a dry ice trap to collect any unconverted methylene chloride and related chlorocarbon species which might arise from degradation or rearrangement of the PCB surrogate. Ion chromatography was used to detect the presence of different organochlorine species and the results are reported in terms of total chlorine. At the end of the test, the melt was rapidly quenched in water. The quenched product, referred to as Ecomelt™, is an environmentally benign product that possess latent cementitious properties. The Ecomelt was subsequently converted into construction-grade cement for beneficial use.

During the test program, waste containing a PCB equivalent of up to 9,300 parts per million (ppm) was tested. No chlorine was detected (at a sensitivity of 25 ppm) in the

product gas in the two tests conducted, indicating that the destruction and removal efficiencies (DRE) exceeded 99.997 percent and 99.996 percent. Samples of Ecomelts were also analyzed for chlorine content. The results showed that up to 73 percent of the chlorine fed to the reactor was retained in the Ecomelt.

The Ecomelt was pulverized and converted into construction-grade cement. This cement was used to prepare 2-inch cubes of mortar for compressive strength determination per ASTM specification C 109. After 3, 7, and 28 days of curing, the compressive strengths were measured to be 2,670 psi, 4,320 psi, and 5,580 psi (each value is an average of triplicate measurements), respectively. The compressive strengths significantly exceed the ASTM requirements for blended cement as well as portland cement (the 3-, 7-, and 28-day compressive strength requirements for blended cement are 1,890 psi, 2,900 psi, and 3,480 psi, respectively; those for portland cement are 1,740 psi, 2,760 psi, and 4,060 psi, respectively). The presence of chlorine in the Ecomelt did not adversely affect the strength of the Cement-Lock cement.

Previous studies conducted at IGT with dredged estuarine sediments at bench- and pilot-scale levels yielded similar results in terms of organic destruction and cement quality. Based on this observation, we predict that the results of PCB destruction and chlorine sequestration tests conducted at larger scales of operation would be similar to those achieved here in the bench-scale study. Thus, we consider the Cement-Lock Technology is to be ready for processing PCB-containing wastes at larger scales of operation.

The Cement-Lock process economics are also very favorable because of the dual revenue streams associated with the process: processing (tipping) fees received for contaminated wastes and revenues received from sale of the construction-grade cement product. The next step is to apply the Cement-Lock Technology for the remediation of specific sites containing high levels of PCBs, such as Superfund sites in the Hudson and Passaic River Basins to demonstrate and confirm its commercial viability.

PCB-containing wastes can be found at numerous Superfund sites, such as the Hudson and Passaic Rivers in the NY/NJ harbor area. Currently, a 30,000 cubic yards

per year capacity Cement-Lock demonstration plant is under construction in New Jersey for treatment of contaminated dredged estuarine sediment. It is recommended that this demonstration plant be utilized to test PCB-laden sediment, perhaps from one of the above listed sites. The objective of this test would be to demonstrate the capability of the Cement-Lock Technology to not only decontaminate these sediments but also to put these sediments to beneficial use by converting them into construction-grade cements. Such a test is also essential to provide a basis for permitting, product utilization, and public acceptance. The larger quantity of cement produced could be used in actual construction projects. This beneficial use aspect of the demonstration would greatly enhance the technical and economical feasibility of the Cement-Lock Technology for entering the broad environmental remediation market.



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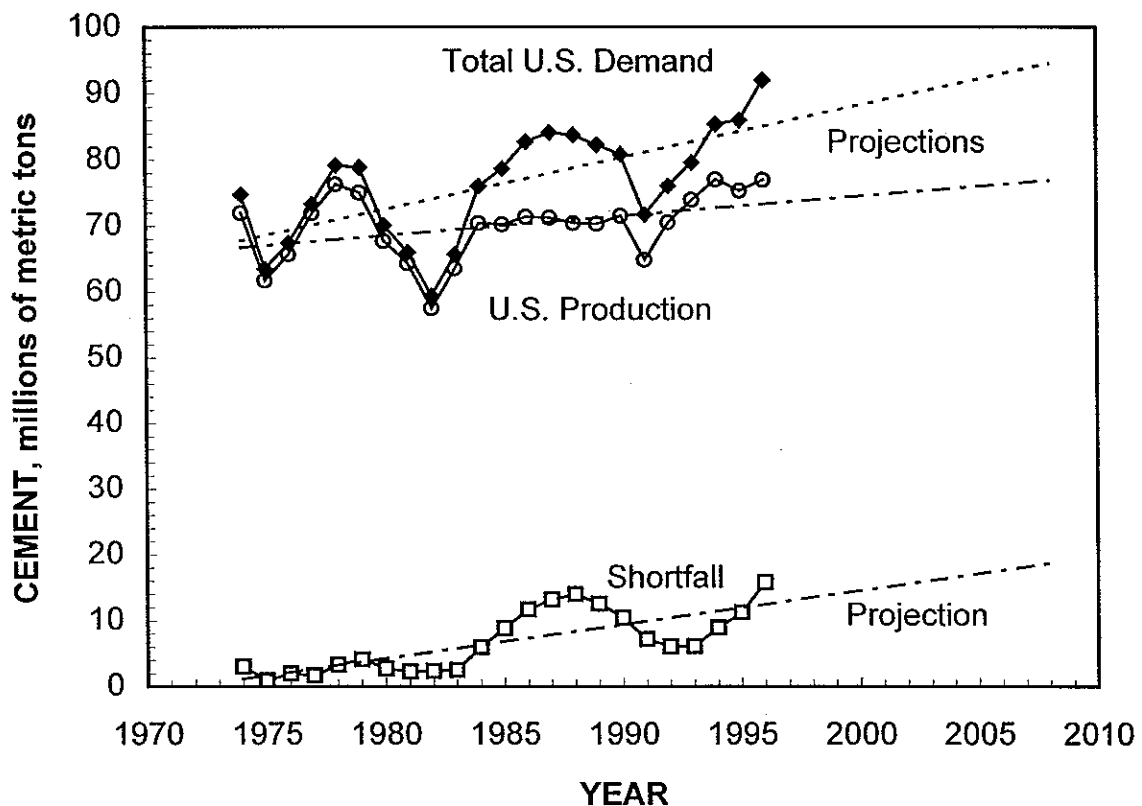
## INTRODUCTION

### Background

Hundreds of tons of PolyChlorinated Biphenyl (PCB)-containing wastes have been accumulating at Superfund sites as well as in canals that once acted as dump sites for industrial wastes. PCB-containing waste oils from transformers are now becoming harder to dispose of. PCBs very easily get into waterways (lakes, ponds, rivers) and are subsequently absorbed by fish tissue. Ultimately, the contaminated fish enter into the food chain with the potential for considerable harm to human health. This has become a major concern for regulators. As an example of the magnitude of this problem, approximately 300 miles of the Erie Canal as well as the Hudson river require treatment of the sediment bed to remediate PCBs which amounts to millions of cubic yards of PCB-containing sediment. Currently, the exorbitant costs associated with just handling the PCB-containing wastes are enough to deter the massive cleanup of these wastes.

The Cement-Lock™ Technology, developed by the Institute of Gas Technology (IGT), offers a one-step solution for treating contaminated materials in which the organic contaminants are completely destroyed, inorganic contaminants are immobilized, and the resultant solid product from the treatment is put to a beneficial use (Business Week, 1997; Baker, 1997; Rehmat *et al.*, 1998). The technology is flexible enough to accommodate the complex and varying nature and levels of contaminants and their widespread spatial distribution within PCB-containing wastes such as those in superfund site soils. The Cement-Lock Technology is capable of simultaneously handling the fixation of heavy metals if these are present, and the destruction of polynuclear aromatic hydrocarbons (PAHs) and organochlorines, such as dioxins, furans, chlorinated pesticides, and herbicides, in addition to PCB. Natural gas is the most suitable source of energy for this recycle and reuse technology. About 5 BCF of natural gas is required to process one million tons of waste. As a beneficial use, Cement-Lock Technology produces cement from contaminated wastes for sale in the merchants market. Cement was selected as a beneficial-use product due to the reasons stated below.

The decline in the infrastructure of the U.S. cement industry is well documented. The United States has gone from being a cement exporting nation in the 60's to a cement importing nation in the 90's due to increasing demand for cement by the construction industry (Figure 1). Demand is rising by an average of about one percent per year – or about 800 thousand metric tons. U.S. production, however, has not kept pace with demand. In 1996, the U.S. cement shortfall was about 15.8 million tons. At this rate of cement demand increase, the cement shortfall in the United States will be well over 150 million tons in the next decade.



**Figure 1. DEMAND AND PRODUCTION OF CEMENT IN THE UNITED STATES**

New cement manufacturing capacity is being added slowly. About 70 percent of U.S. cement manufacturing facilities are over 25 years old. Exorbitant construction costs, environmental regulations, and increased cost of raw materials and energy – compounded by stagnant cement prices due to imports – are major reasons for the stifled growth in the

cement industry. Conditions are not expected to improve until new and innovative ideas are implemented that provide attractive returns for manufacturers.

The Cement-Lock Technology offers an outstanding solution to revitalize the cement industry infrastructure at a fraction of the capital cost, while utilizing raw materials and wastes that actually generate revenues from their use. Thus, a supplemental cement supply can be produced and sold at prices comparable to or less than those of the conventional portland cement.

The Cement-Lock Technology, which has been demonstrated with dredged estuarine sediment (sponsored by Brookhaven National Laboratory in collaboration with industry), dredged river sediments [sponsored by the Gas Research Institute (GRI) and the Michigan Department of Environmental Quality], and contaminated concrete (sponsored by GRI) (Rehmat *et al.*, 1998, 1999), is an excellent candidate to not only remediate these PCB-containing wastes, but also to put these wastes to beneficial use. The Cement-Lock Technology destroys the organic contaminants, immobilizes the inorganic contaminants into an amorphous solid matrix, and converts the wastes into cement for general construction applications. The Cement-Lock Technology uses natural gas as fuel. The intent is to make the technology applicable to a wide array of contaminated feedstocks so that the supply of raw material to the plant can be assured. The resulting industry can be sustained for a long period of time; the associated consumption of natural gas can also be assured for a similarly long period.

Although there are similarities in the treatment of dredged estuarine sediment and PCB-contaminated sediment and wastes, there were enough differences to justify undertaking an exploratory research program to determine the efficacy of the process for this particular application. For example, the PCB content of the dredged estuarine sediment is below the regulatory limit (currently 50 mg/kg), whereas the PCB content of some PCB-contaminated sediments are on the order of 1 to 5 weight percent, and therefore, are classified as hazardous. As a result, inadequate destruction in the latter becomes unacceptable.

Also, because of low PCB concentrations, chlorine sequestration in dredged estuarine sediment is not an issue. For PCB-containing sediments and wastes, however, in-situ sequestration of chlorine is extremely important to prevent formation of dioxins at the discharge end of the process. Such issues require alterations to the process to make it suitable for this particular application.

### **Program Objectives**

The objectives of this proposed research were to determine the extent of PCB destruction in PCB-containing wastes by the Cement-Lock Technology (using methylene chloride as a surrogate), and to determine the fate of chlorine present in PCB. Another objective was to demonstrate beneficial use of these wastes by producing construction-grade cement having strength properties that meet or exceed ASTM (American Society for Testing and Materials) requirements.

### **Program Success Criteria**

The following criteria were established to measure success of this research program:

- The destruction of PCB in the waste must exceed 90 percent.
- At least 50 percent of chlorine present in the PCB-containing waste must be sequestered in the Ecomelt™.
- Compressive strength of cement produced from the Ecomelt must pass ASTM standards for portland cement.

This report presents the results of an experimental program conducted by IGT under a contract with GRI for "Remediation and Beneficial Reuse of PCB-Containing Wastes Using the Cement-Lock Technology." Construction Technology Laboratories, Inc. (CTL, Skokie, IL - the research arm of the Portland Cement Association) was a subcontractor to IGT on the project to confirm standard properties for the Cement-Lock end product.

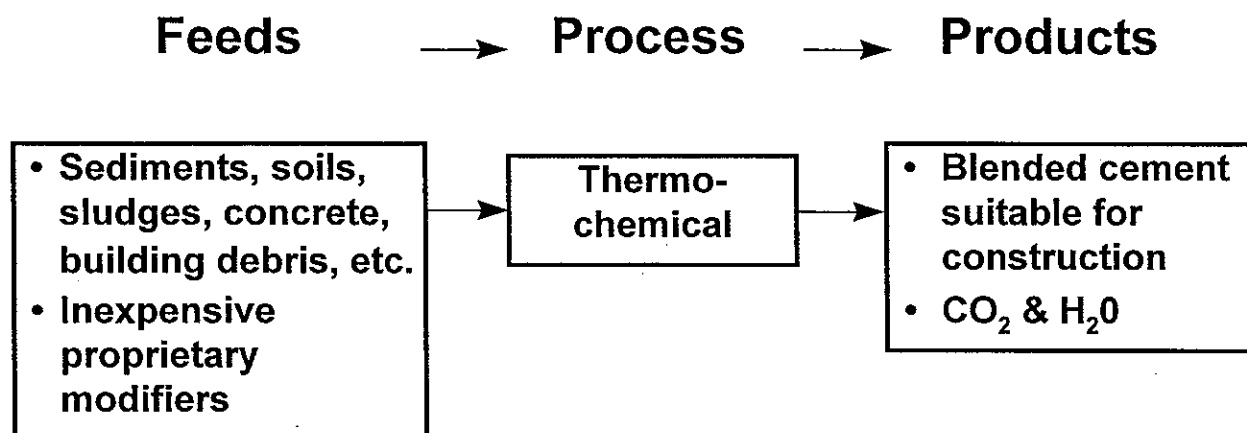
## **CEMENT-LOCK TECHNOLOGY DESCRIPTION AND BENEFITS**

The Cement-Lock Technology is an advanced management system for contaminated soils, sediments, sludges, concrete and building debris, and similar wastes. This technology systematically puts every ounce of waste to beneficial use. The Cement-Lock Technology converts the waste into a construction-grade cement, which can be sold in the open market. All secondary and fugitive waste streams associated with typical waste processing are completely eliminated. Additional beneficial products that could be produced depend upon the waste stream and its composition. In the case of contaminated sediments, in addition to producing cement, it could also produce steam for power generation.

The beneficial use of wastes through Cement-Lock Technology application adds many advantages to conventional waste processing. These include a) additional revenues generated from the sale of cement; b) savings from the elimination of the need to landfill the wastes, including sizable quantities of residues from conventional processing; c) ability to maintain extremely low tipping fees because of secondary revenue streams; and d) environmental superiority when compared to any conventional processing.

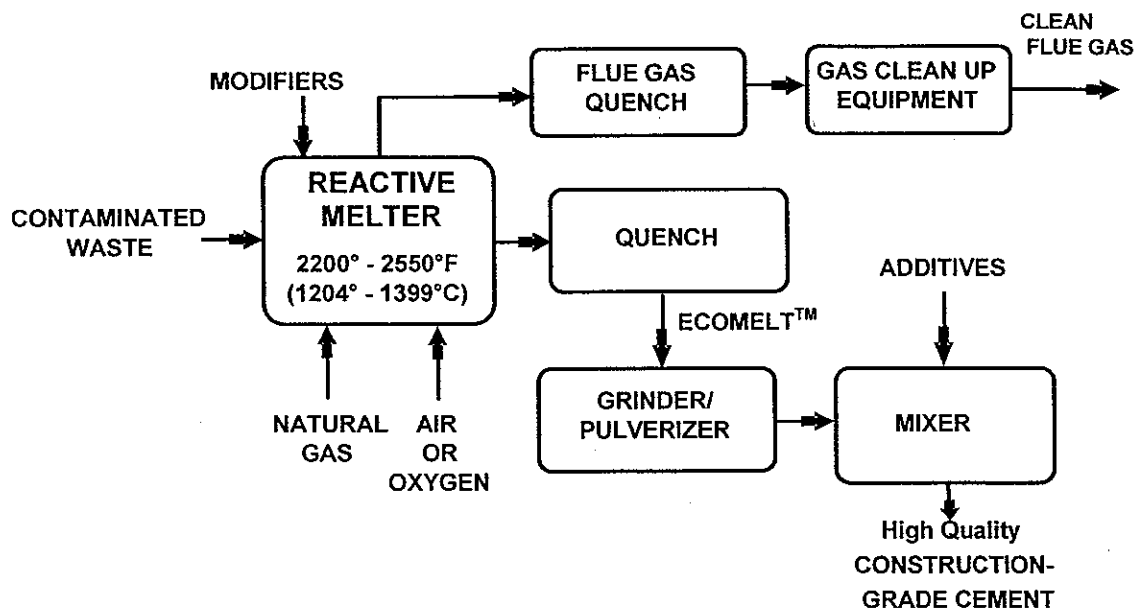
The Cement-Lock Technology is not to be confused with either the cement manufacturing plants or incineration technologies. With only the final product as a common element, the Cement-Lock Technology bears no other relationship to the manufacture of portland cement. The Cement-Lock Plant is considerably simpler than a portland cement manufacturing plant and bears little or no resemblance to the actual complex cement plant. Unlike a cement plant, the Cement-Lock Technology does not have an extensive sizing requirement for the materials being processed, it does not have the extreme temperature requirements of a cement plant, it does not produce any waste stream (such as cement kiln dust), it does not require complex energy management to save energy, it does not produce high NO<sub>x</sub> emissions, it does not have stringent requirements for materials of construction, and finally the starting raw materials are entirely different.

Nor is the Cement-Lock Technology an incineration process either. It is rather a thermo-chemical manufacturing process that utilizes inherent properties of wastes as feedstocks for producing economically attractive end products (Figure 2).



**Figure 2. CEMENT-LOCK = MANUFACTURING PROCESS**

In the Cement-Lock Technology (Figure 3) contaminated wastes are reacted in a melter with suitable modifiers in proportions required for producing an environmentally friendly material called, "Ecomelt". Ecomelt is a decontaminated and environmentally stabilized product that possesses latent cementitious properties. These properties are utilized to convert the Ecomelt into construction-grade cement, which has compressive strength properties exceeding those required for conventional portland cement. The melter for carrying out this process is operated at temperatures up to about 2550°F (1399°C), or lower temperatures sufficient to melt the waste-modifier mixture. In the presence of excess air at these temperatures, organic contaminants originally present in the waste are completely destroyed and converted to innocuous carbon dioxide and water. Chlorine present in some of the organic compounds (such as dioxins, furans, and PCBs) is converted to hydrogen chloride (HCl), which is either sequestered in the melt or readily scrubbed from the flue gas by using a solid media filter comprised of calcium oxide operating at 1000° to 1100°F (538° to 593°C).



**Figure 3. CEMENT-LOCK TECHNOLOGY SCHEMATIC DIAGRAM FOR PROCESSING CONTAMINATED WASTES**

Heavy metals present in the wastes are locked into the cement matrix (predominantly calcium-alumino silicates) to completely immobilize them. The melt containing immobilized metals is rapidly quenched to prevent crystallization and subsequently pulverized and mixed with an additive to yield cement. This product can be put to beneficial use in the construction industry with a ready market. Volatilized heavy metals as well as non-destroyed organics are recovered from the gas and recycled to the melter for complete assimilation in the process. Highly volatile metals, such as mercury and arsenic, are removed from the off-gas by amalgamating them with affinity metals distributed over a filter element.

Hot flue gas emanating from the melter is used to preheat the modifiers before they enter the melter. The modifiers also act as a filter to remove particulates from the flue gas. The flue gas is quickly cooled from about 2550° to 1600°F (1399° to 871°C) in the filter. Additional heat can be recuperated from the flue gas to raise steam.



The Cement-Lock Technology does not generate any secondary hazardous waste streams. The streams exiting the process are: 1) construction-grade cement as a primary product, 2) a solid stream consisting of  $\text{CaCl}_2$  and  $\text{CaSO}_4$  (with small amounts of  $\text{NaCl}$  and  $\text{KCl}$ ) as a secondary product usable as winter road salt, 3)  $\text{CO}_2$  and water vapor, and 4) an amalgam of Hg.

The advantages of the Cement-Lock Technology include:

- a. It can treat all types of contaminated (organic as well as inorganic) materials regardless of its concentration.
- b. It treats all types of soils - from sandy to clayey and silty.
- c. No feed pretreatment is required.
- d. No secondary hazardous waste streams are generated from the process.
- e. It is an environmentally friendly technology.
- f. It is a simple - yet effective process.

The following benefits accrue from deployment of the Cement-Lock Technology:

- It provides a sound basis for destroying harmful organic contaminants and immobilizing inorganic contaminants present in wastes.
- It utilizes wastes to produce a widely used salable product (construction-grade cement) thereby conserving land-based resources which would have otherwise been deployed.
- It helps defray the costs of waste cleanup whereby resources could be deployed elsewhere for environmental restoration.
- It does not discharge environmentally harmful pollutants into the atmosphere.
- The product from the waste treatment is environmentally safe to use in the construction industry.
- Although the technology is thermo-chemical in nature, it offers much superior destruction of organic contaminants than any known incineration technology.

The Cement-Lock Technology can be applied to remediation of contaminated sediments, contaminated soils at Superfund sites as well as manufactured gas plant sites and recycling of contaminated concrete. Besides cleaning up waste sites, the technology offers a great potential for additional job creation and economic enrichment in affected communities.

The technology has no known limitation in terms of application with respect to types of contaminants or the levels of contaminants. It has no limitations on water content of the waste stream either.

The Cement-Lock Technology can handle a variety of feedstocks; these feedstocks are summarized in Tables 1 and 2. Primary feedstocks (Table 1) include sediments, soils, sludges, concrete, fly ash, bottom ash, cement kiln dust, etc. Secondary feedstocks (Table 2), such as petroleum coke, used rubber tires, refinery bottoms, paper mill sludge, etc., contain fuel value and can be co-processed with primary feedstocks.

**Table 1. PRIMARY FEEDSTOCK CANDIDATES FOR CEMENT-LOCK TECHNOLOGY**

Feedstock	Category	Water Content Limit, wt %	Limit on Type and Extent of Organic Contaminants	Limit on Type and Extent of Inorganic Contaminants
Dredged estuarine sediments, Cat. I, II, III	Nonhazardous	Up to 70%	None	None
Contaminated soil from Superfund sites	Hazardous	n/a	None	None
Contaminated soil from town gas sites	Nonhazardous	n/a	None	n/a
Sludge from Superfund sites	Hazardous	Up to 70%	None	None
PCB-Contaminated sediments	Hazardous	Up to 70%	None	n/a
Construction debris	Hazardous	n/a	None	None
Contaminated concrete from DOE and DOD decommissioning	Hazardous	n/a	None	None
Fly ash and bottom ash	Hazardous & Nonhazardous	n/a	n/a	None
Spent FCC catalyst	Hazardous	n/a	None	None
Cement kiln dust	Hazardous	n/a	n/a	None

**Table 2. SECONDARY FEEDSTOCK CANDIDATES FOR  
CEMENT-LOCK TECHNOLOGY**

Waste Stream	Category	Reason for Being a Waste Stream	Limit on Organic Contaminants for Cement-Lock Application	Limit on Inorganic Contaminants for Cement-Lock Application
Used rubber tires	Nonhazardous	Difficult to burn in combustion systems, produces dioxins, furans, SO <sub>x</sub> , etc.	None	None
Municipal sewage sludge	Hazardous	High metal content	None	None
PCB-Contaminated transformer oils	Hazardous	PCB content	None	n/a
Refinery bottoms	Nonhazardous	High sulfur and metals	None	None
Petroleum coke	Nonhazardous	High sulfur and vanadium	None	None
Coal washings (Culm)	Nonhazardous	High sulfur, high ash	None	None
Paper mill sludges	Hazardous	Dioxins	None	None
Gas from sewage treatment plant	Nonhazardous	high sulfur, low calorific value	None	n/a
Waste organic stream from chemical plant	Hazardous & Nonhazardous	Difficult to dispose	None	None

## **BENCH-SCALE TESTS FOR DESTRUCTION OF PCB AND FATE OF CHLORINE**

The Cement-Lock Technology has been tested successfully for generating Ecomelt with a mineral composition suitable for producing construction-grade cement. The reactive melter operates at somewhat lower temperature and higher silica content than is typical of conventional rotary kilns producing portland cement. It was proposed that the melt in the Cement-Lock melter could capture chlorine present in PCB-containing wastes (solid, gas, or liquids) and, therefore, detoxify hazardous wastes while deriving fuel values from them. Thermochemical equilibrium modeling supported this possibility.

This section describes laboratory testing of the Cement-Lock melt as a sorbent for chlorine gases derived from destruction of chlorocarbons, such as PCB. Natural gas was burned in air containing a chlorocarbon surrogate for PCB. The gas was bubbled through the melt so that HCl in the combustion products could interact with the minerals. Chlorine and hydrogen chloride were measured in the off-gas. Calcium chloride and alkali chlorides condensed from the off-gas were measured, along with chloride content of the Ecomelt. The chlorine balance was calculated based on these measurements. The Ecomelt was pulverized and prepared for use in cement, so that its compressive strength can be measured. Unconverted chlorocarbons were collected in dry ice traps to calculate the destruction and removal efficiency (DRE).

### **Solid Feed Mixture**

Solid feeds to produce composition specific to the Cement-Lock melts were made up from pure or nearly pure compounds, shown in Table 3. The talc analysis does not show 1.4 percent other minerals, which are present in minor concentration.

Four different mixtures were used during the test program, as is shown in Table 4. The Type 1 mixture was selected to represent a melt fairly high in silica. It was expected that this mixture would be relatively easy to melt. However, this mixture was more

difficult to melt than expected, so Types 2 through 4 mixtures included minor amounts of calcium fluoride as a flux to lower melting point of the mixture. During initial testing, analysis of condensed salts indicated that sodium chloride is formed which accounts for most of the volatile chloride salts. In order to promote retention of chlorine in the melt, sodium compounds were deleted from the mixture Types 3 and 4. The Type 4 mixture is distinguished by its higher calcium oxide content, which is more typical of the midrange of cement melts.

**Table 3. COMPOSITION OF SOLID FEED COMPONENTS**

Compound	Diatomite	Quick Lime	Alumina	Rouge	Talc	Sodium Bicarbonate	Fluorite
	wt %						
SiO <sub>2</sub>	99.75				61.49		
CaO		74.8					
Al <sub>2</sub> O <sub>3</sub>			99.86				
Fe <sub>2</sub> O <sub>3</sub>				99.26	1.65		
MgO					30.54		
Na <sub>2</sub> O						36.9	
CaF <sub>2</sub>							100
loss on ignition	0.25	25.2	0.14	0.74	4.95	63.1	0

**Table 4. SOLID FEED MIXTURES TESTED**

Compound	Type 1	Type 2	Type 3	Type 4
	wt %, fired and normalized*			
SiO <sub>2</sub>	39.8	39.7	39.9	35.4
CaO	48.6	48.4	48.7	53.2
Al <sub>2</sub> O <sub>3</sub>	5.0	5.0	5.0	5.0
Fe <sub>2</sub> O <sub>3</sub>	5.0	5.0	5.0	5.0
Na <sub>2</sub> O	0.6	0.6	0	0
CaF <sub>2</sub>	0	.35	.35	.35
Ratio: CaO/SiO <sub>2</sub>	1.22	1.22	1.22	1.50

\* neglecting interaction with gas.

### Gas Feed Mixture

It is not practical to use PCB mixtures in laboratory experimentation. They are too toxic, difficult to meter accurately, and disperse uniformly in the air. Therefore, a surrogate chlorocarbon was chosen to represent PCB. This chlorocarbon is methylene chloride (or dichloromethane;  $\text{CH}_2\text{Cl}_2$ ). It has a boiling point of 104°F (40°C), so it readily evaporates into the larger volume of air fed during the test. The methylene chloride was delivered from a syringe pump at a controlled rate. The volume delivered was accurately measured by calibrations on the syringe pump barrel which was made from a burette fitted with a piston. Natural gas mixed with air and methylene chloride vapor entering the furnace. The proportion of natural gas was calculated so that the adiabatic flame temperature of the mixture was close to the furnace temperature setting. Therefore, the incoming gas neither heated nor cooled the melt. Injection of  $\text{CH}_2\text{Cl}_2$  was adjusted so that it yielded the equivalent of about 1 percent or 10,000 ppm of PCB in the waste. Typical design feed gas proportions at room temperature and one atmosphere are as follows:

Natural gas	32 ml/min
Air	736 ml/min
Methylene chloride	19 ml/min vapor = 0.050 ml/min liquid

Air and natural gas flows were measured by rotameter-type flow meters. Product gas was similarly measured during Tests 7 through 9.

### Cement-Lock Ecomelts

Solid feed mixtures were packed into 500 ml crucibles made from high purity aluminum oxide. Because of its low bulk density, less than 400 g of this powder could be packed into a crucible. The melt is very corrosive even to pure aluminum oxide. Therefore, fusion times were limited to about 45 min to avoid leakage of melt from corroded crucibles into the furnace.

After bubbling the feed gas through the melt for a measured period, gas flow was stopped, the crucible was removed, and the melt was rapidly quenched by pouring it into

water. The crucible was then dropped into water, shattering it and allowing for the separation of some additional Ecomelt.

The Ecomelt (solidified melt) material was separated from crucible pieces by hand. The amount of Ecomelt recovered was usually less than the theoretical amount due to an Ecomelt coating inside the crucible wall. However, sometimes the Ecomelt recovery was slightly greater than the theoretical amount due to dissolution of aluminum oxide from the crucible and from the gas inlet and outlet tubes. After drying, the Ecomelt was coarsely crushed in a steel mortar and pestle to pass 20 mesh (841 microns). It was then ball milled for approximately 80 min with 1-inch berrundum media. This produced a powder coarser than that used in cement, with approximately 50 percent passing 200 mesh (74 microns). This degree of fineness assures good mixing, so that samples withdrawn for analysis are representative of the whole. During the final 20 min of ball milling, the powdered Ecomelt was removed and collected on a filter by entrainment in flowing air.

### **Experimental Method**

The details of experimental set up and methods used for product analyses are given below.

#### **Equipment Setup**

Figure 4 shows the arrangement of experimental apparatus, including the gas sampling system. The furnace is lined with a 6-in ceramic tube x 36 in. high which confines and controls the experimental atmosphere. A movable pedestal, which is mounted in the lower end cover of this containment tube, supports the crucible. This pedestal is moved upward into position to seal the crucible with the crucible lid, and it is rotated manually to provide some stirring and mixing. The entire pedestal with the crucible mounted in it is removed from the furnace to quench the melt.

Eight Kanthal electric heaters totaling 6 kW surround the experimental hot zone of the furnace. A clamshell heater directly below that provides supplemental heat and

As of Test 6

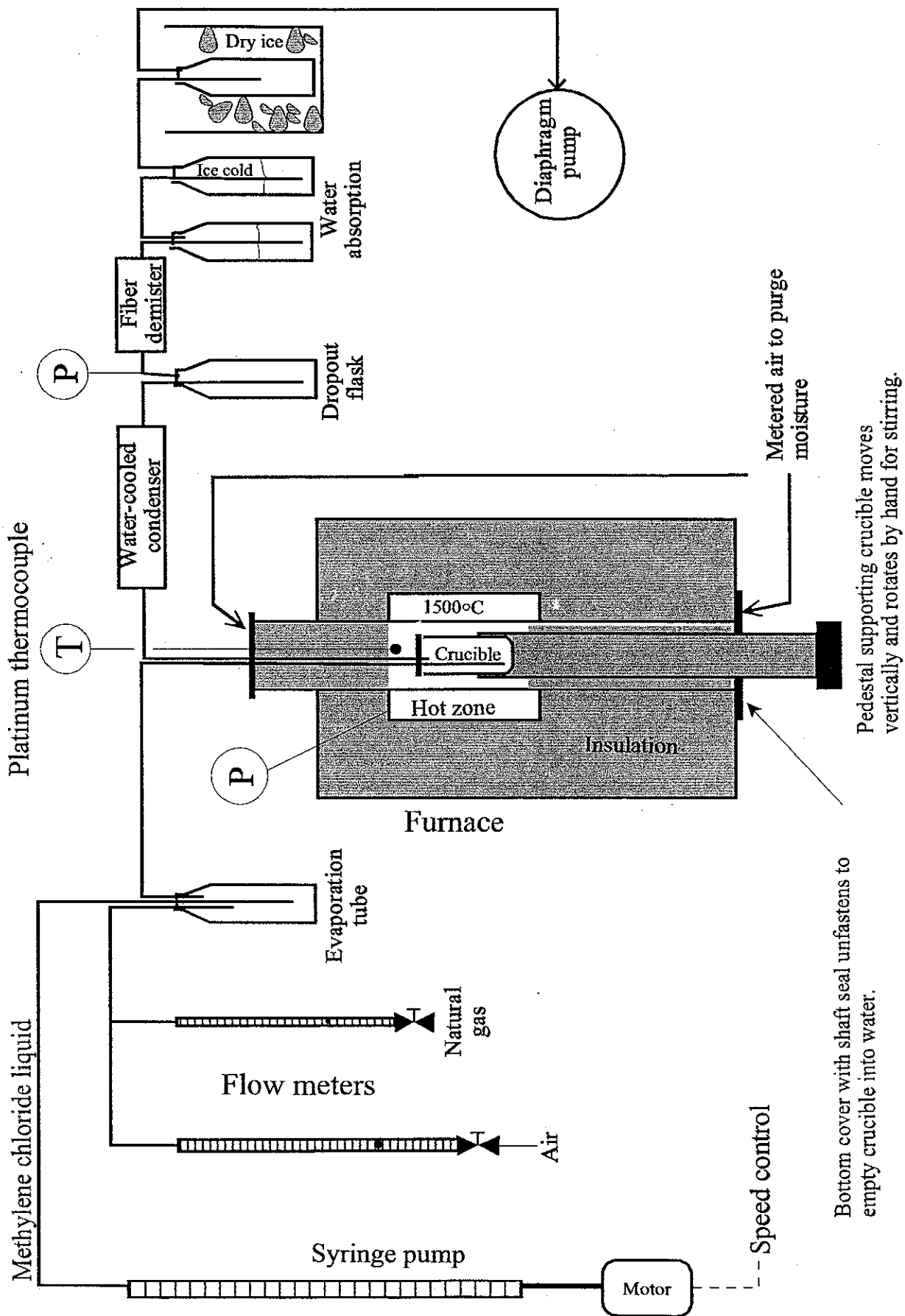


Figure 4. EXPERIMENTAL APPARATUS FOR PCB DESTRUCTION TESTING



avoids thermal shock of the pedestal and containment tube. Both heaters are controlled by Digital PID controllers. The hot zone temperature is sensed by a type R platinum thermocouple mounted directly above the crucible lid. Its controller readout is verified by a separate digital meter.

The lid on the crucible makes it roughly air tight, and purge air at the upper and lower ends of the furnace assures that all product gases are swept into the exhaust tube centered in the crucible lid. This ceramic exhaust tube connects with a pyrex exhaust tube at the upper cover of the containment tube. This tube feeds into a glass condenser and then into a dropout bottle. Vaporized salts condense in the glass and ceramic exhaust tubes, the condenser, and the dropout bottle. Product gas then passes through 2 or 3 bubblers containing pure water where any remaining hydrogen chloride is separated from the gas. In Tests 6 through 8, the product gas then passed through a dry ice trap to collect any unconverted chlorocarbons. The arrangement shown in Figure 4 corresponds to Test 6. Variations used in other tests are noted under the section "Test Details."

### **Analysis of Products**

**Chloride in Ecomelt and Solid Feeds.** 2 g of Ecomelt powder is weighed into a 30 ml Teflon beaker. 18 ml of 4 normal nitric acid is mixed with the Ecomelt powder. The beaker is covered with Teflon and heated to 180°F (82°C) for an hour with stirring. 6 ml of 48 percent hydrofluoric acid is added while stirring with the Teflon rod. The covered mixture is heated at 180°F (82°C) for at least eight more hours. The slurry is then neutralize to pH 5.5 using methyl red indicator to avoid attack on glass fiber filters by residual hydrofluoric acid. The slurry is filtered on Whatman 40 paper and the filtrate is treated with 8 ml of 2 percent silver nitrate solution, precipitating silver chloride. This precipitate coagulates and becomes easy to filter after an hour of gentle heating. It is then filtered on a borosilicate glass fiber filter and rinsed. 10 ml of 4 normal nitric acid is added to the filter funnel and allowed to stand without suction. This eliminates silver phosphate or oxide or any other acid-soluble impurity. After rinsing thoroughly, the filter is fired for 30 min at 1202°F (650°C) and weighed.

Raw feed mixtures were analyzed by the same method as described above. Feed Types 1 through 3 contained 0.012 millimoles of chlorine per gram of raw feed mixture. Feed Type 4 contained 0.010 millimoles of chlorine per gram of feed. These are equivalent to 0.043 wt% and 0.035 wt%, respectively.

**Chloride in Offgas.** Insides of the glass and ceramic exhaust tubes, condenser, and dropout bottle are extracted with distilled water and the volume of these extracts is measured. A measured fraction of the filtered extract is treated with silver nitrate solution, coagulated and filtered on borosilicate glass fiber with a nitric acid rinse, as is done in the Ecomelt analysis for chlorine. This procedure measures total chloride, which is distributed among hydrochloric acid, and the chlorides of calcium, alkali metals and possibly iron and magnesium.

**Cation Analysis.** Hydrochloric acid in the product gas system extract is measured by titration against 1.0018 normal sodium hydroxide.

Iron chlorides are measured in combination gravimetrically. Any ferrous salt is oxidized to the ferric state by treatment with a few ml of 3 percent hydrogen peroxide. The solution is then neutralized to pH 8 with ammonium hydroxide to precipitate ferric oxide, filtered on ashless paper, fired, and weighed. Only traces of iron salts are usually found.

Calcium is measured gravimetrically by precipitation with potassium oxalate. The calcium oxalate precipitate is filtered on ashless paper, which is fired in a crucible at 1202°F (650°C). This is treated with a few drops of sulfuric acid to convert the calcium to sulfate which is again fired at 1202°F (650°C) to render it stable and unreactive toward atmospheric moisture.

Alkali metal chlorides are also measured gravimetrically by difference. A portion of the gas sampling system extract is evaporated to dryness and weighed. Its calcium and iron chloride content are known from the foregoing analyses, and are subtracted from the total weight. The remaining alkali chloride salt is reported as sodium chloride. Sodium chloride is the predominant chloride salt vaporized into the gas stream.

**Analysis for Molecular Chlorine.** A small amount of potassium iodide is added to the gas sampling system extract, followed by starch indicator. This is titrated with standard sodium thiosulfate solution until the blue color disappears.

### **Test Details**

A total of nine high-temperature experiments were conducted inside the atmosphere furnace; the methods and results are described below. Successive modifications to equipment setup are described with each experiment. Since the purpose varied from one experiment to the next, reported results and reporting format also vary. Conditions and results for all of the nine tests are briefly summarized in Table 5.

#### **Test 1**

The objective of the first experiment was to test equipment operation and to determine approximate melting temperature of the solid feed mixture. No methylene chloride was fed into the reactor; only air and natural gas were fed. Type 1 feed powder was heated for 50 min at 2500°F (1371°C) followed by 15 min at 2642°F (1450°C).

When the furnace was opened after the test, there was a lot of moisture inside the upper and lower ends of the containment tube. It arose as a combination of combustion products from the natural gas, and initial burnout of organic binders in the new ceramic fiber insulation. In addition, the ceramic exhaust tube had shattered, apparently due to heat shock from downward flow of condensate into the hot zone. The feed powder did not fuse but had only sintered.

After the first test, the furnace was modified to avoid future problems with condensed water. The discharge end of the exhaust tube was bent at an angle to prevent back flow of condensate into the reactor, and its vertical inlet section was insulated to suppress condensation. Water cooling of the copper containment tube covers was discontinued. Metered flows of air were added at the upper and lower containment tube covers to purge water vapor and prevent liquid water draining onto the hot ceramic.

Table 5. SUMMARY OF TEST RESULTS

Test No.	Solid Feed Type <sup>a</sup>	Feed Solids, g	Temp, °F	Test Duration, min	PCB Surrogate CH <sub>2</sub> Cl <sub>2</sub> fed, ml	Natural Gas Rate, ml/min	Combustion Air Rate, ml/min	Purge Air Rate, ml/min	Expected Ecomelt, Amount g	Ecomelt Collected, g	Feed Chlorine Captured in Ecomelt <sup>b</sup> , %	CH <sub>2</sub> Cl <sub>2</sub> DRE <sup>c</sup> , %	Comments
1	1	294	2642	15	0	30	710	0	229	n/a	n/a	n/a	Equip shutdown & test for fusion temp. Condensate shattered ceramic internals. No fusion occurred.
2	1	62	2642	230	0	30	710	0	62	n/a	n/a	n/a	Semi-fused. Verified type R TC output with a type K TC.
3	1	294	2921	105	3?	31	880	8.6	250	lost	n/a	n/a	Air purges added at top and bottom. Melt dissolved crucible & damaged furnace.
4	1	355	2804	60	3.03	33	700	15.4	302	247	16 <sup>b</sup>	n/a	Crucible leaked melt. Ecomelt Cl analysis questionable. Low Cl capture due to presence of Na.
5	2	368	2730	30	1.56	33	710	59	313	332	20 <sup>b</sup>	n/a	Ecomelt and cation distribution analyzed. Gas by passed the melt. Low Cl capture due to presence of Na.
6	3	376	2730	25	1.65	30	600	71	322	332	73	>99.997	Melt plugged gas inlet tube. Containment tube broke from suction.
7	4	396	2730	27	1.0	50	710	82	310	310	37	>99.996	Increased feed CaO. Gas flow erratic. Forced/induced draft combined.
8	4	393	2642	38	1.85	32	710	80	345	345	23	not analyzed	Melt ate hole in side on gas inlet. Much gas bypassed the melt.
9	none	0	2730	60	0	50	0	750	0	0	n/a	n/a	Blank test (No CH <sub>2</sub> Cl <sub>2</sub> fed). Explained surpluses in chlorine balances.

a See Table 4 for details.

b Excess chlorine appeared in gas-borne products due to vaporization from furnace refractories. Ecomelt chloride is likely underestimated in Tests 4 and 5 due to a problem with analytic method.

c DRE = Destruction and removal efficiency.

Before each test, the containment tube is tested to verify that it is air tight. Therefore, the only way for gas to exit the reactor is through the ceramic exhaust tube. Air purges enter the crucible where it joins the lid or where gas inlet and outlet tubes penetrate the lid with narrow annular clearance, mix with reaction product gases, and are carried out through the gas sampling system.

To verify the temperature measurement, the furnace was operated at 2012°F (1100°C) with a type K shielded thermocouple to verify output from the type R thermocouple used in the hot zone control. They agreed within approximately 1 percent, and the type K thermocouple reading was slightly higher, showing that the type R thermocouple did not underestimate the true temperature.

### **Test 2**

A small 90 ml crucible was filled with 62 g of Type 1 feed which had been recovered from Test 1. This material was heated to 2642°F (1450°C) for three hours and 50 min, then allowed to cool inside the closed furnace. The cooled sample spontaneously shattered into many pieces. Its upper surface was smooth and steeply concave. Its inner surfaces showed many large interconnected pores but small pores were absent. Its condition was transitional between sintered and fused. Because of the strongly oxidizing conditions in these tests, iron in the melt is entirely ferric (trivalent) and melting point is elevated relative to neutral or reducing conditions. Crucible walls showed moderate corrosion by the melt even though it had not fused. Already, it was apparent that it would be difficult to fuse this mineral mixture without dissolving its container.

### **Test 3**

In the third test, methylene chloride flow commenced for the first time. The amount of methylene chloride delivered was not metered.

The temperature setting was 2948°F (1620°C), however, the temperature control was erratic because the furnace current limit needed to be set higher. Consequently, temperatures during the test period was as low as 2876°F (1580°C).

After 105 min at high temperature, the pedestal was lowered to remove the crucible. This was difficult because the melt had dissolved the crucible wall and escaped into the furnace pedestal and elsewhere. After some effort, most of the crucible came loose and was dropped into water. The pedestal assembly and furnace internals were damaged and had to be replaced. Premium insulation was ordered to allow for continuous operation as hot as 3002°F (1649°C). Ecomelt produced during this test was not analyzed.

In addition, the ceramic exhaust tube had broken again. It is believed that this was again caused by condensed water, and it was avoided in later tests by increasing the flow of purge air to the containment tube upper end, especially during preheat.

#### **Test 4**

During the first four tests, twin pairs of water bubblers were used in the gas sample system, with an upstream switching valve to select either set. This arrangement proved to be unreliable during the fourth test because condensed solids obstructed the switching valve and made gas flow difficult to control. The condensed solid may have been smoked from final burnout of refractories, or more likely, alkali chloride salt from the reaction. The twin sets of gas bubblers had been intended to study saturation of the melt with chlorine which would be reflected in relatively higher chloride in the exhaust gas later in a test compared with the earlier period during the same test. Sample switching with a valve proved to be difficult and unreliable, so it was abandoned in later tests.

The dropout bottle, shown in Figure 4, had not been used in the first three tests. It was added during Test 4 about 20 min after the start of that test, and it reduced problems with condensed solids and acidic liquid downstream in the gas sampling system.

Type 1 feed was heated for 60 min at a temperature of 2804°F (1540°C). The flows of methylene chloride, air and natural gas were held near their planned values. The crucible was removed intact and its contents were poured into water, but by then the crucible had begun to leak, and again furnace internals were damaged by the melt.

Nevertheless, the fourth test produced scientifically useful data. The gas sampling system was analyzed for chloride, calcium, total salts, and acidity as described above; results are shown in Table 4. Calcium chloride accounted for 1.8 percent of the total chlorine input, while the alkali (sodium and potassium) chlorides accounted for 22 percent of the chlorine input. Thus, sodium dominated salt vaporization, even though calcium was far more abundant.

During the first four tests, the glass exhaust tube had not yet been installed; and a stainless steel exhaust tube and condenser were used instead. Analysis of the vaporized product from Test 4 showed that the stainless steel was substantially attacked by hydrogen chloride present in the product gas. Therefore, pyrex glass tube, instead of stainless steel tube, was used in the later tests. This also eliminated an extraneous source of iron and chromium in reaction products.

Product Ecomelt was found to contain 0.16 percent chloride, which accounted for 16 percent of chlorine fed during this test. However, this was probably an underestimate, because analytic methods had not yet been perfected at that time. Residual hydrogen fluoride attacked the glass fiber filters used to separate silver chloride. This resulted in underestimates of chloride in Ecomelts produced during Tests 4 and 5. Also, chloride present in the water bubblers was not analyzed. Subject to these caveats, chlorine distribution is given in Table 6. The total chlorine in the products exceeded total chlorine in the feed. As described later, Test 9 was conducted in which the furnace was fired to 2730°F (1499°C) with no mineral feeds. This test showed that chlorine was produced from the furnace materials or natural gas, and helps explain the surplus in chlorine balance.

Cation analysis of combined volatile products gave 1.83 milliequivalents of calcium, 21.8 milliequivalents of alkali metal, and 16.1 milliequivalents of hydronium. Salts were found principally in the exhaust tubes and condenser, while hydrochloric acid was found principally in the dropout bottle.

**Table 6. DISTRIBUTION OF CHLORINE IN TEST 4 PRODUCTS**

Sample	Chlorine atom, millimoles	Percent of feed chlorine
Methylene chloride	94.7	95.7
Feed solid powder	4.2	4.3
<b>Total chlorine input</b>	<b>98.9</b>	<b>100.0</b>
Product Ecomelt	16.0	16.2
Ceramic exhaust	8.2	8.2
S.S. exhaust	23.0	23.2
Condenser	24.8	25.0
Dropout bottle	59.4	60.1
Bubblers A & B free Cl <sub>2</sub>	0.2	0.2
Hose to diaphragm pump	0.6	0.7
<b>Total chlorine output</b>	<b>132.2</b>	<b>133.6</b>

### Test 5

In the fifth test, a small amount of calcium fluoride (CaF<sub>2</sub>) was added to the solids feed mixture to reduce its melting temperature and promote melting. The amount of calcium fluoride added was calculated to match typical iron blast furnace practice, and amounted to 0.35 percent. High purity calcium fluoride reagent was used in this test as well as all succeeding tests; it contains less than 0.05 percent chloride. Addition of this flux was successful in reducing the fusion temperature to below 2732°F (1500°C), but the flux also accelerated the attack by melt on ceramic materials, so fusion time periods were still limited to less than 50 min.

The products of combustion from the mixture of air, methylene chloride and natural gas were bubbled through the molten material for 30 min of its total 40 min of test duration at high temperature. Chloride in the product gas was collected in pure water in a single pair of bubblers during that 30 min period. The melt eroded the gas inlet tube, perforating it so that the gas bypassed the melt after approximately 30 min.

The molten material was removed from the furnace after 40 min at a temperature of 2730°F (1499°C). It flowed rapidly from the crucible when pouring into water. After



quenching in water, the solidified melt (Ecomelt) was shiny and vitreous, with essentially no internal void.

Products of the fifth test were analyzed in greater detail than from the previous tests so as to study distribution of the chloride and cations; the chloride and cation distributions are given in Table 7.

Total alkali metals in volatile products were equivalent to 81 percent of the sodium blended into the feeds as sodium bicarbonate. However, additional alkalis may have been present as impurities in other feed solid components.

**Table 7. FEED AND PRODUCT ANALYSIS FROM TEST 5**

	Cl <sup>-</sup>	H <sup>+</sup>	Na <sup>+</sup>	Ca <sup>+2</sup>	Fe <sup>+3</sup>	total cations
	← total millimoles chloride-equivalent →					
Feed solid powder	4.4		>63.2			
Methylene chloride	48.7		0			
<b>Total in feeds</b>	<b>53.1</b>		<b>&gt;63.2</b>			
Ecomelt	>14.1	0	NA*	NA	NA	NA
Ceramic exhaust	21.9	0.15	22.8	0.054	0.28	23.9
Pyrex exhaust	2.4	1.2	1.7	0.050	0.065	3.2
Condenser & tube	2.5	1.7	1.3	0.029	0.055	3.2
Dropout bottle	15.5	11.3	7.0	0.10	0.14	18.9
Water bubbler A	7.7	1.9	9.5	0.17	0.09	12.0
Water bubbler B	7.6	0.8	9.1	0.10	0.12	10.5
<b>Total in products</b>	<b>71.7</b>	<b>17.05</b>	<b>51.4</b>	<b>0.503</b>	<b>0.75</b>	<b>71.7</b>

\*NA = Not analyzed.

Sodium accounted for 72 percent of total cations condensed from the off gas. Hydronium ion derived from hydrogen chloride gas accounted for 24 percent, and together hydronium, and sodium amounted to 96 percent of the volatile cations.

According to these data, chlorine is found principally in product gas as vaporized sodium chloride when sodium cations are present in the melt. However, the goal for these tests was to maximize chlorine retention in the Ecomelt, therefore, the feed minerals

should be low in sodium and potassium content. For that reason, sodium bicarbonate or other alkali metal compounds were not added to the solid feed mixtures after Test 5.

Free chlorine was not detected in Test 5 products by the starch-iodine method.

Melting and boiling points of metal chlorides are tabulated in Table 8 in order of declining alkalinity of the metal. All the chlorides which may potentially be formed from metals in feeds are included, whether they actually form or not. Ferrous chloride is the most volatile of these species, while magnesium and iron chlorides are not stable under hot oxidizing conditions. Chlorine appears to associate with the alkali metals sodium and potassium, which are the strongest bases available. Consequently, it is the alkali chlorides, which has been principally found in the condensate, along with minor amounts of calcium chloride. If sodium content in the feed is reduced, then chlorine content of the Ecomelt will increase along with hydrogen chloride content of the product gas.

**Table 8. MELTING AND BOILING POINTS OF POTENTIAL METAL CHLORIDE PRODUCTS**

Species	Melting point, °F (°C)	Boiling point, °F (°C)
KCl	1418 (770)	2732 (1500)
NaCl	1474 (801)	2575 (1413)
CaCl <sub>2</sub>	1440 (782)	~ 3524 (~1940)
MgCl <sub>2</sub>	1317 (714)	2574 (1412)
FeCl <sub>2</sub>	1242 (672)	1875 (1024)

### **Test 6**

One of the goals of this project was to determine whether half of total chlorine in the feeds could be sequestered in the Ecomelt. In Test 6, a feed mixture was prepared without addition of sodium bicarbonate. This mixture was otherwise similar to feeds used in all testing to date. The mass ratio of calcium oxide (CaO) to silicon dioxide (SiO<sub>2</sub>) remained at 1.22. This is at the acidic end of the range of lime/silica ratios (C/S), which are suitable for producing cements. Mixtures, which are higher in lime, are more alkaline and are expected to retain chlorine more effectively than the present Ecomelt.

Therefore, if the melt in this test retains half of chlorine input, it is reasonable to expect that the entire range of lime/silica ratios will perform as well or better. The high-lime end of the melt range is about C/S=1.64. Published phase diagrams show that fusion temperatures rise with increasing lime-to-silica ratio.

The test was terminated after 25 min due to difficulty in maintaining steady gas flow. The melt intermittently obstructed the gas inlet, becoming more severe near the end of the test.

Chlorine found in the Ecomelt amounted to 73 percent of the total chlorine in solid feed plus methylene chloride feed. The amount of chlorine retention further increases if the Ecomelt chlorine is compared with just chlorine present in the methylene chloride feed. Thus, an important project goal was achieved.

Because of difficulty in the Ecomelt analysis noted above, it was not immediately clear that chlorine retention had exceeded 50 percent. For that reason, two more tests (Tests 7 and 8) were conducted. Results of Tests 7 and 8 were not as useful as Test 6 due to operational difficulties. A ninth test was conducted in which the furnace was fired to 2730°F (1499°C) with no mineral feeds. Test 9 showed that chloride was produced from the furnace materials or natural gas, and helps explain systematic surpluses in the chlorine balances.

Test 6 also included a dry ice trap to collect any unconverted chlorocarbons which might be present in the product gas. The dry ice trap is simply an empty flask cooled by dry ice at the downstream end of the gas sampling system (see Figure 4). After Test 6, the dry ice trap contained a few ml of frozen water with no visible organic matter. The water was extracted with 2 ml of cyclooctane. After filtration through 0.45 micron media, this organic extract was analyzed for chlorine by ion chromatography. No chlorine was detected at a sensitivity of 25 parts per million (ppm), so the most chlorocarbon which may have survived passage through the reactive melt is  $3.4 \times 10^{-5}$  wt fraction of the organic chlorine in the methylene chloride feed. This corresponds to a destruction and removal efficiency of 99.997 percent.

After the melt had been removed during Test 6, pressure in the containment tube accidentally declined from near atmospheric to less than half atmospheric. This caused the containment tube to crack horizontally at two levels, dividing it into equal thirds. To cope with potential leaks at these sites, Tests 7 through 9 were operated in combined induced draft and forced draft modes, maintaining pressure at the crucible very close to atmospheric by manual adjustment of valves.

### Tests 7 and 8

As noted above, because of difficulty in the chlorine analysis in the Ecomelt, it was not immediately clear that chlorine retention had exceeded 50 percent during Test 6. For that reason, two more tests (Tests 7 and 8) were conducted.

The feed material for Test 7 differed from Test 6 in that a higher lime-to-silica ratio (C/S) was used. The C/S weight ratio was increased from 1.22 to 1.50. Surprisingly, this mixture melted just as easily as the mixture used in Test 6.

Test 7 lasted only 27 min due to inability to maintain steady gas flows and atmospheric reaction pressure. In this test the ceramic exhaust tube was obstructed due to condensation of chloride salts. Variations in the flow and reaction pressure were chaotic, rather than cyclical. The exhaust-throttling valve was adjusted by hand continuously in an attempt to hold reaction pressure near atmospheric. Only 37 percent of chlorine fed to the system was captured by the Ecomelt. It is likely that some of the chlorine in the feeds escaped during periods of greater than atmospheric reaction pressure. To prevent any future recurrence, a new appliance was assembled to vacuum out and collect any solid obstructions from the ceramic exhaust while the furnace is in operation.

Frost collected in Test 7 dry ice trap was extracted into 3 ml of cyclooctane. Analysis by ion chromatography detected no organochlorine compounds at a sensitivity of 25 ppm. This means that the chlorocarbon survival wt fraction must be less than  $3.8 \times 10^{-5}$ , which corresponds to a DRE of at least 99.996 percent.

Operating conditions in Test 8 were the same as in Test 7 except that the temperature setting was 2642°F (1450°C) instead of 2730°F (1499°C). Test 8 solid feed also corresponds to Type 4 proportions with a lime-to-silica mass ratio of 1.5.

There was a 15 min interruption during Test 8 due to a check valve clogging with condensed chloride salts. As a result, the crucible was at the experimental temperature for about 50 min rather than the typical 35 min. The crucible was very thin at the time melt was poured into water but had not yet begun to leak. Crucible removal and melt pouring into water went smoothly; it was recorded on a videotape.

The low viscosity observed while pouring the melt suggests that it may be possible to further lower the operating temperature. This should improve chlorine retention in the melt, while reducing corrosion of ceramic materials.

Because of the delay at the high temperature, the melt had a longer than usual time to attack the ceramic gas inlet tube. It apparently developed a hole in one side, about halfway through the test period. This was detected by a change in behavior of the natural gas flow meter float. It normally vibrated several times per second as gas bubbles were released from the inlet tube discharge submerged in the melt. When vibration stopped, it indicated that the incoming feed gas bypassed the melt. As a result, melt gas contact was poor during Test 8, and the chlorine retention was only 23 percent compared to 73 percent in Test 6. The dry ice trap was used in Test 8, but the material collected in that trap was not analyzed for chlorocarbons because chlorine retention in the Ecomelt was below target.

During the chlorine analysis of Test 8 Ecomelt, it was discovered that the glass filters used to separate silver chloride were slightly attacked by residual hydrofluoric acid used to leach the minerals. A series of tests were conducted to determine what pH adjustment was necessary to suppress reaction with the glass. The hydrofluoric acid-bearing leach solution was partially neutralized with NaOH to pH of 3.5, 4.5, 5.5 and 6.5. After standing in these solutions for 5 min, the glass filter media were rinsed, dried, and weighed. It was found that the weight was unchanged at pH of 5.5 and above. Therefore, adjustment to a pH of 6.0 was selected for the standard analytic procedure.

Analyses for Ecomelts and feed materials for Tests 6 to 8 reflect measurements at a pH of 6.0. Replicate analyses of the Ecomelts show that these analyses are reproducible within about  $\pm 6$  percent.

### Test 9

In earlier tests, the amount of chlorine found in the products exceeded the amount of chlorine in the feed (for example, see Tables 6 and 7). Test 9 was conducted in an effort to resolve this discrepancy. The furnace was operated without crucible, methylene chloride feed, and any solid feeds. Therefore, the chlorine input was zero and any chlorine in the outputs must arise from either the furnace materials or from the natural gas feed. Results in Table 9 show that indeed substantial chlorine appeared in the products. The cation analysis shows that hydrogen chloride was the principal chlorine-bearing species under these conditions, in contrast to Test 5 results in which sodium chloride dominated.

**Table 9. CHLORIDE AND CATIONS IN PRODUCTS  
WITH NO CHLORINE IN FEED**

	Cl <sup>-</sup>	Na <sup>+</sup>	H <sup>+</sup>	Ca <sup>+2</sup>	Fe <sup>+3</sup>
	← total millimoles chloride equivalent →				
Ceramic exhaust through dropout bottle	12.6	3.28	11.2	0.25	0.04
Bubblers A & B	2.4	0.85	3.6	0.35	0.00

Phosphates are sometimes used as inorganic binders for the types of fiber refractories in our furnace. A question arose whether such phosphates might vaporize and cause interference in the chloride analyses by co-precipitation of silver phosphate.

The liquid extracts from Test 9 were tested for phosphates by precipitation of calcium phosphate from a neutral solution. Only a trace of phosphates was found. In addition, a known amount of calcium phosphate was added to a chloride assay to determine whether it caused interference or overestimate of chloride content. The nitric

acid rinse used in the analytic procedure dissolved calcium phosphate completely, therefore, there was no such interference.

It was concluded that chloride was retained on the furnace walls when methylene chloride was introduced in the furnace. The chlorine was subsequently released yielding more chlorine in the product than in the feed.

### **Significant Test Results**

The following significant results were derived from tests conducted for the destruction of PCB surrogate and sequestration of the resulting chlorine species:

1. The quantity of methylene chloride ( $\text{CH}_2\text{Cl}_2$  - PCB surrogate) fed to the system was equivalent to yielding 9,300 ppm of PCB in the waste feed. Chlorocarbons in the off gas, surviving the reactive melt contact, were undetected at a sensitivity of 25 ppm. This amount is equivalent to PCB destruction and removal efficiency (DRE) exceeding 99.996 percent.
2. Measurements showed that 73 percent of chlorine present in the feed was sequestered in the Ecomelt.
3. Addition of 0.35 percent calcium fluoride flux reduced fusion temperature substantially. A temperature of 2642°F (1450°C) is more than adequate to melt a typical Cement-Lock Ecomelt composition.
4. Corrosion of ceramic materials by the melt was unavoidable at the laboratory scale. However, it can be avoided at industrial scale by maintaining a thermal gradient and a layer of solidified melt between the reactor refractories and the molten material.
5. Calcium amounted to less than 2 percent of cations vaporized even when feeds were low in sodium. The addition of sodium to the feed materials reduced calcium vaporization still further even though calcium was present in feeds in far greater amount than sodium. Vaporization of iron was insignificant and sometimes undetectable. Alkali metals sodium and potassium dominated the volatile chlorides

when they were present in significant amount in the feeds. When the alkalis were deficient, hydrogen chloride gas dominated chlorine species in the products.

6. Free molecular chlorine ( $\text{Cl}_2$ ) was undetectable in one test and found in trace amount in another test. Chlorine in the product gas was negligible in this process concept.



## **CONVERSION OF PCB-CONTAINING WASTES INTO CONSTRUCTION-GRADE CEMENT**

This section consists of results obtained from the characterization and evaluation tests conducted by the Construction Technology Laboratories, Inc., (the research arm of the Portland Cement Association) on the Ecomelt samples produced during PCB destruction and chlorine sequestration tests conducted under conditions promulgated by the Cement-Lock Technology. During this testing, the products of combustion from a mixture of methylene chloride (a PCB surrogate), natural gas, and excess air were passed through the reactive melt; the methylene chloride was completely destroyed and a significant amount of chlorine present in the methylene chloride was sequestered by the melt.

### **Characterization of Ecomelt**

Approximately 1000 g sample of the Ecomelt was submitted to CTL for characterization and evaluation as a suitable material for producing construction-grade cement.

The Ecomelt sample was a dry, fine-grained material, almost passing through a 100 mesh (149 microns) sieve. The Ecomelt was analyzed by X-ray fluorescence (XRF) method for major and minor oxides content; the results are summarized in Table 10. The Ecomelt contained 42.79% of CaO, 27.95% of SiO<sub>2</sub>, and 21.55% of Al<sub>2</sub>O<sub>3</sub>, with moderate amount (5.12%) of Fe<sub>2</sub>O<sub>3</sub>.

### **Determination of Glassy Phase in Ecomelt**

The Ecomelt was examined for the glassy phase content using an optical microscope (with transmitted light) as well as X-Ray diffraction (XRD) methods. These procedures determined both the crystalline and glassy phase contents in the material.

**Table 10. OXIDE ANALYSIS OF ECOMELT**

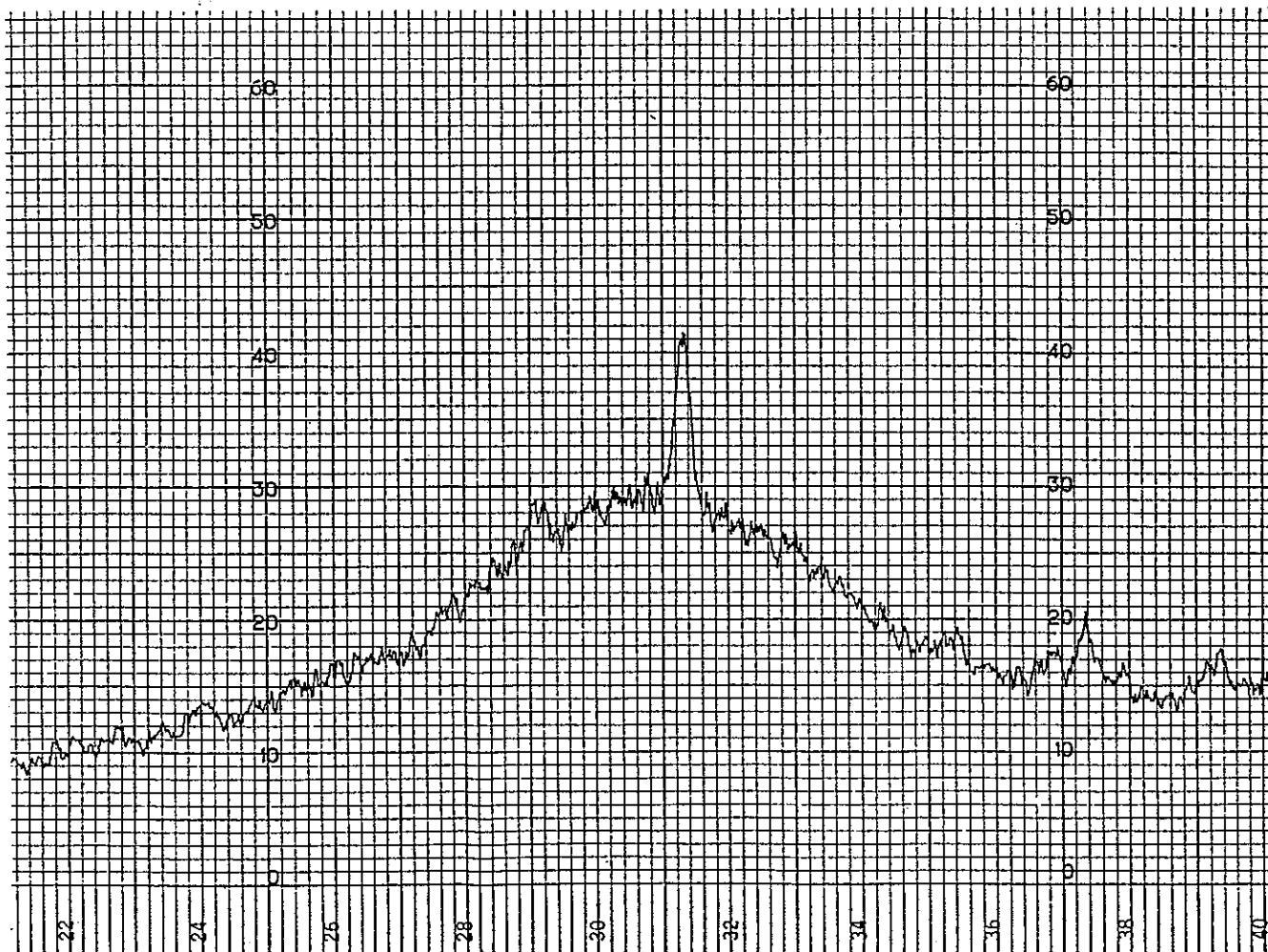
Analyte	wt %
SiO <sub>2</sub>	27.95
Al <sub>2</sub> O <sub>3</sub>	21.55
Fe <sub>2</sub> O <sub>3</sub>	5.12
CaO	42.79
MgO	1.28
SO <sub>3</sub>	<0.01
Na <sub>2</sub> O	0.61
K <sub>2</sub> O	0.02
TiO <sub>2</sub>	0.06
P <sub>2</sub> O <sub>5</sub>	0.04
Mn <sub>2</sub> O <sub>3</sub>	0.01
SrO	0.01
Loss on Ignition	0.22
Total	99.68

#### **Microscopic Test**

A small sample of the finely ground Ecomelt was examined under an optical microscope using both ordinary and cross-polar lights, and the amount of glass phase in the sample was estimated visually. Under ordinary light, both amorphous (glassy) as well as crystal phases are visible, however, under cross-polar light, the amorphous phase is not visible. It was estimated that the Ecomelt was nearly 95 percent glassy. The conchoidal fracture of the Ecomelt, their clarity, and homogeneity also confirmed the glassy nature of the material.

#### **X-Ray Diffraction (XRD) Test**

The ground Ecomelt was also examined for its glassy phase content using XRD method. The existence of a broad hump and absence of any noticeable peaks from the XRD-pattern (Figure 5) confirmed that the Ecomelt was primarily of a glassy nature. Typically, the presence of peaks in an XRD pattern refer to crystalline compounds, whereas a broad hump is attributed to the glassy nature of material.



$2\theta$  ( $\text{CuK}\alpha$ )

**Figure 5. XRD PATTERN OF ECOMELT SHOWING AMORPHOUS PHASE**

### Preparation of Construction-Grade Cement

The Ecomelt was finely ground in a ball mill to a Blaine fineness of over 4100 cm<sup>2</sup>/g (4184 cm<sup>2</sup>/g to be precise). The ground material was then blended with an additive in a 40:60 proportion by weight (i.e., 40 percent Ecomelt + 60 percent additive), to produce construction-grade cement. No activator (performance enhancing material) was used.

### Testing and Evaluation of Cement

Using the cement prepared above and Ottawa sand, a mortar mix was prepared in accordance with ASTM C 109 standard mixing procedure. The mix water was used such that the water-to-cement weight ratio was 0.484, which gave a mortar flow of 112. The mortars were cast as 2-inch cubes and left overnight in a moist room at ambient temperature. Thereafter, the cubes were demolded and cured in saturated lime-water solution. As per ASTM specification C 109, the cubes were tested for compressive strength after 3, 7, and 28 days of curing (for each time period, three samples were tested); the results are summarized in Table 11. The measured average compressive strength of the cement after 3, 7, and 28 days of curing was 2,670 psi, 4,320 psi, and 5,580 psi, respectively.

**Table 11. COMPRESSIVE STRENGTHS OF MORTARS PREPARED FROM PCB-CONTAMINATED WASTE-BASED CEMENT\***

Test Period, days	Total Load 1, lbs	Total Load 2, lbs	Total Load 3, lbs	Average Load, lbs	Average Strength, psi	ASTM Requirements	
						ASTM 150 (Type I), psi	ASTM 595 (Type IP), psi
3	10,300	10,600	11,100	10,670	2,670	1,740	1,890
7	17,500	17,200	17,100	17,270	4,320	2,760	2,900
28	22,600	23,000	21,300	22,300	5,580	4,060	3,620

\*water/cement wt ratio = 0.484, flow = 112.

The compressive strength data of the mortar cubes indicate that the cement acquired noticeably higher 3-, 7-, and 28-day strengths than both the ASTM C150 Type I portland cement and ASTM C 595 Type IP blended cements requirements (the 3-, 7-, and 28-day compressive strength requirements for blended cement are 1,890 psi, 2,900 psi, and 3,480 psi, respectively; those for portland cement are 1,740 psi, 2,760 psi, and 4,060 psi, respectively). The presence of chlorine in the Ecomelt did not adversely affect the strength of the Cement-Lock cement.

### **Significant Test Results**

The glassy nature of the Ecomelt observed by an optical microscopic as well as XRD tests strongly suggests that the material produced from the PCB destruction and chlorine sequestration tests is of pozzolanic nature. Higher compressive strengths than those required by ASTM C 150 specification for portland cement and by ASTM C 595 specifications for blended cements confirm these observations. Furthermore, the presence of chlorine in the Ecomelt did not adversely affect strength of the cement products.

## ACHIEVEMENT OF PROGRAM SUCCESS CRITERIA

The following criteria were established to measure success of this research program:

- The destruction of PCB in the waste must exceed 90 percent.
- At least 50 percent of chlorine present in the PCB-containing waste must be sequestered in the Ecomelt.
- Compressive strength of cement produced from the Ecomelt must pass ASTM standards for portland cement.

In this program, the following were demonstrated:

- The solid waste was fed with chlorocarbon equivalent to 9,300 ppm of PCB, of which greater than 99.996 percent was destroyed under conditions specified for the Cement-Lock Technology.
- 73 percent of chlorine was sequestered by the reactive melt formed by solid carrier for PCB. The solid carrier consisted of about 50 percent calcium oxide; the balance consisted of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$ , and  $\text{Al}_2\text{O}_3$ . For effective capture of chlorine, the weight ratio of  $\text{CaO}/\text{SiO}_2$  was greater than 1.4.
- The Ecomelt produced from the solid carrier for PCB-containing waste was transformed into construction-grade cement which yielded compressive strengths of 2,670 psi, 4,320 psi, and 5,580 psi after 3, 7 and 28 days of curing. The compressive strengths significantly exceed the ASTM requirements for blended cement as well as portland cement (the 3-, 7-, and 28-day compressive strength requirements for blended cement are 1,890 psi, 2,900 psi, and 3,480 psi, respectively; the requirements for portland cement are 1,740 psi, 2,760 psi, and 4,060 psi, respectively). Thus, the presence of chlorine in the Ecomelt did not adversely affect strength of the cement product.

## RECOMMENDATIONS

Based on results of the bench-scale studies presented in this report, it is concluded that the Cement-Lock Technology is suitable for remediating PCB-containing wastes. PCB-containing wastes can be found at numerous Superfund sites, such as the Hudson and Passaic Rivers in the NY/NJ harbor area. However, a demonstration of the Cement-Lock Technology on actual PCB-containing wastes would be essential to provide a basis for permitting, product utilization, and public acceptance.

Currently, a 30,000 cubic yards per year capacity Cement-Lock demonstration plant is under construction in New Jersey for the treatment of contaminated dredged estuarine sediment (Rehmat *et al.*, 1999). It is recommended that this demonstration plant be utilized to test PCB-laden sediment, perhaps from one of the above listed sites. The objective of this test would be to demonstrate the capability of the Cement-Lock Technology to not only decontaminate these sediments but also to put these sediments to beneficial use by converting them into construction-grade cements. The larger quantity of cement produced could be used in actual construction projects. This beneficial use aspect of the demonstration would greatly enhance the technical and economical feasibility of the Cement-Lock Technology for entering the broad environmental remediation market.

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